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# Thermal induced structural transformation of bimetallic AuPd nanoparticles

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**Abstract.** High Angle Annular Dark Field Scanning Transmission Electron Microscope (HAADF-STEM) has been employed for the study of thermal effects of structural transformation of AuPd nanoparticles produced by physical vapour deposition. Depending on the duration of annealing at a temperature of 500 K, atomic resolved imaging analysis reveals the formation of various structure morphologies from the ordered  $L1_2$  superlattice to the core-shell structure. The effects of Pd-oxides are also discussed.

## 1. Introduction

Bimetallic AuPd nanoparticles have received considerable attention in recent years partly due to their potential applications in nanocatalysis and fuel cells. In order to design and produce nanoparticles with tailored properties, understanding of the interplay of thermodynamics and kinetics in nanoparticle formation is essential. Theoretically, the structure and chemical ordering of AuPd nanoparticles have been investigated [1-3]. Due to the lower surface energy of Au against Pd, in general surface segregation of Au is favoured, resulting in  $\text{Pd}_{\text{core}}\text{Au}_{\text{shell}}$  chemical structure. However, depending on how AuPd nanoparticles are synthesized, experimental observations of  $\text{Au}_{\text{core}}\text{Pd}_{\text{shell}}$  as well as mixed phases have been reported in the literature [4-7]. Here, kinetics may play an important role in structure formation, apart from other external factors such as molecule adsorption. In this paper, we report our recent study on effects of thermal annealing on size, structure and chemical ordering of bimetallic AuPd nanoparticles prepared by physical vapour deposition (PVD). Our goal is to gain a better understanding of the formation mechanisms of various AuPd nanoalloys.

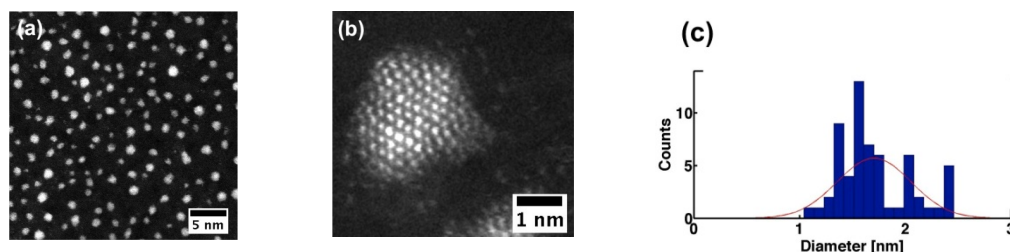
## 2. Experimental details

The AuPd nanoparticles were produced via PVD on amorphous carbon thin film-covered transmission electron microscopy (TEM) grids under high vacuum conditions ( $\sim 10^{-7}$  mbar). Pd atoms were deposited first, followed by deposition of Au. The substrate temperature was held at 300 K during the deposition. Subsequent annealing was carried out at a temperature of 500 K. A 200 kV JEM 2100F scanning transmission electron microscope (STEM), fitted with a CEOS probe corrector for spherical aberration, was employed to image the nanoparticles. All images were recorded using a camera length of 10 cm, which corresponds to an inner collection angle of the high angle annular dark field (HAADF) detector of 62 mrad.



### 3. Results and discussions

Figure 1 (a) and (b) show typical HAADF-STEM images of AuPd nanoparticles deposited onto amorphous carbon at 300 K. It was observed that the nanoparticles do not show any clear evidence of phase segregation. This is in line with expectations from most of the previous calculations [1-2]. An analysis of the size distribution of AuPd nanoparticles in Figure 1 (c) shows a mean diameter of  $1.70 \pm 0.34$  nm.



**Figure 1** (a, b) Low and high magnification HAADF-STEM image of as-deposited AuPd nanoparticles onto amorphous carbon substrate maintained at 300 K. (c) Diameter distribution of AuPd nanoparticles in (a).

Type	60 minutes	120 minutes	180 minutes
Mixed	(a)	(b)	N/A
Layered	N/A	(c)	(e)
Core-shell	N/A	(d)	(f)

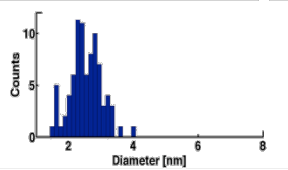
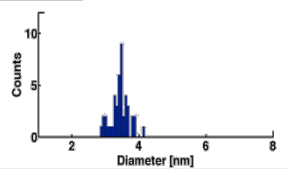
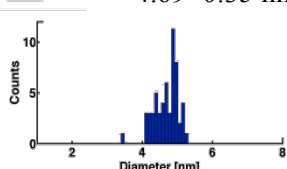
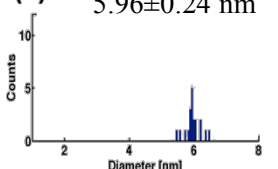
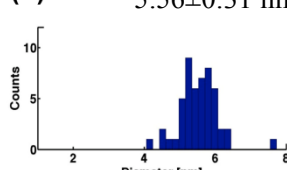
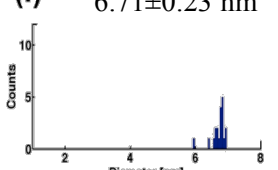
**Figure 2** HAADF-STEM images of AuPd nanoparticles annealed at 500 K in situ, for: (a) 60 minutes; (b-d) 120 minutes, and (e-f) 180 minutes.

When the sample was annealed at a temperature of 500 K for 60 mins, a well-ordered alloyed phase of the AuPd nanoparticles could be observed, as shown in Figure 2 (a). Examining the fast fourier transform (fft) pattern of the HAADF-STEM (shown in the inset) reveals the existence of secondary spots in the forbidden positions. The structure can be attributable to  $L1_2$  superlattice [7,8]. The particle in Fig. 2 (a) is aligned along the  $\langle 100 \rangle$  zone axis, with pure Au columns alternating with Au and Pd columns in their two-dimensional projection, as marked by the yellow arrow pointers. The image contrast can be attributed to the difference in the atomic numbers of the constituent elements ( $Z_{Au}=79$ ,  $Z_{Pd}=46$ ) [9].

Further annealing of the sample at 500 K up to 120 mins resulted in other nanoparticles morphologies, as shown in Fig. 2 (b-d). Fig. 2 (b) shows a nanoparticle with the same  $L1_2$  superlattice as in Fig.2 (a), but aligned in the  $\langle 110 \rangle$  zone axis. In the layered morphology case, a thin layer can be seen surrounding the exterior of the AuPd nanoparticles, as marked by the arrow pointers in Fig.2(c). The height of this layer is about 2-3 atomic Pd layer using isolated single Pd atoms as mass standard. We attribute this layer to the formation of Pd-oxide layer. A closer inspection of the lattice spacing of Pd revealed a value of  $0.30 \pm 0.01$  nm, which is larger than the nearest neighbour distance of Pd. Possible causes for the dilation of the Pd lattice include the incorporation of either oxygen or carbon into the lattice during the annealing process [10]. No such ordered thin layers were observed for Pd-only particles that had been annealed under the same condition.

For the 120 min.-annealed sample, nanoparticles with core-shell structures were also observed as shown in Fig. 2 (d). The darker contrast core in the images indicate that the structure has a Pd-rich core and Au-rich shell, in agreement with the energetic consideration that Pd has a lower surface energy and slightly higher cohesive energy than that of Au.

**Table 1.** Diameter distribution for AuPd nanoparticles annealed in situ at 500 K for (a) 60 minutes; (b-d) 120 minutes and (e-f) 180 minutes, respectively.

Type	60 minutes	120 minutes	180 minutes
Alloyed	(a) $2.53 \pm 0.28$ nm 	(b) $3.43 \pm 0.27$ nm 	N/A
Layered	N/A	(c) $4.69 \pm 0.35$ nm 	(e) $5.96 \pm 0.24$ nm 
Core-shell	N/A	(d) $5.56 \pm 0.31$ nm 	(f) $6.71 \pm 0.23$ nm 

**Table 2.** Evolution of nanoparticles density as a function of annealing time

Time of annealing	As deposited	60 minutes	120 minutes	180 minutes
Density (particles/ $\mu\text{m}^2$ )	$5.18 \times 10^4$	$3.95 \times 10^4$	$1.69 \times 10^4$	$1.39 \times 10^4$

Previously, Marical *et al.* showed that a very small concentration of CO molecules in the air could be sufficient enough to lead a structural transformation from  $\text{Pd}_{\text{core}}\text{Au}_{\text{shell}}$  to  $\text{Au}_{\text{core}}\text{Pd}_{\text{shell}}$  [11]. In the present study, the annealing was conducted under the vacuum condition before the nanoparticles were exposed to air prior imaging. No structure reversal was observed during e-beam irradiation. This could be because the prolonged annealing has already driven the nanoparticles to a thermodynamic stable configuration that has trapped the Pd in the core. We also observed that the core-shell structure was only observed for those particles with large sizes (see Table 1).

To correlate the thermal induced structure transform with size, we analysed nanoparticle size distribution. The results are shown in Table 1. It is apparent that not only had the annealing process caused the structure transformation, but it also resulted in an increase in the nanoparticles' size. As the annealing time increased from 60 to 180 minutes, the mean diameter increased from  $2.53 \pm 0.28$  nm to  $6.71 \pm 0.23$  nm. At the same time, the density of the nanoparticle decreased from  $5.18 \times 10^4$  particles/ $\mu\text{m}^2$  to  $1.39 \times 10^4$  particles/ $\mu\text{m}^2$  (see Table 2). These values suggest that nanoparticles growth during annealing took place via coalescence or Oswald ripening. It is possible that the ordered  $\text{L1}_2$  superlattice is only possible for small size nanoparticles. It is also interesting to note that, for the prolonged 180 minutes annealing, no nanoparticles with the ordered  $\text{L1}_2$  superlattice had been observed, indicating that the structure may have been trapped into a thermodynamic metastable state.

#### 4. Conclusions

In summary, we have performed a systematic investigation of atomic structure of AuPd using HAADF-STEM. Upon annealing at an elevated temperature, we show that the AuPd nanoparticles undergo a rich structural transformation, from randomly mixed phase as-deposited to an ordered superlattice and Pd-rich core/Au-rich shell configuration. We have also established a close correlation between the observed structures and the nanoparticle sizes. Our results highlight the paramount importance of understanding the intricate relationships between energetics and kinetics in bimetallic nanoparticle formation for exploring their potential novel applications.

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